

Electron Correlations and Moment Sum Rules*

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(Received 1 November 1972)

A theory of electron correlations based on a generalized random-phase approximation is presented. An expression for the local-field correction is obtained using the third frequency moment of the spectral function of the electron-density response function. The local field is a functional of the structure factor $S(\vec{q})$ which in turn is related to the imaginary part of the dielectric function via the fluctuation-dissipation theorem. The equations are self-consistently solved to determine $S(\vec{q})$ as originally suggested by Singwi *et al.* The pair-correlation function, compressibility, plasma dispersion, and correlation energy of electron liquid at metallic densities have been calculated.

I. INTRODUCTION

In this paper we have used exact sum rules to study electron correlations at metallic densities. The wave-vector- and frequency-dependent dielectric function describes the response of an electron liquid to an external probe coupled to the density fluctuations in the system and is related to the density-response function. The coefficients in the asymptotic expansion of the density-response function in powers of $1/\omega$ are the frequency moments of its spectral function. The low-order moments of this function are known.^{1,2} We have used the usual mean-field expression for the density-response function. The form of the effective mean field is obtained by *satisfying* the third frequency moment of the spectral function of the density-response function. The effective mean field is a functional of the static structure factor $S(\vec{q})$, which in turn is related to the imaginary part of the inverse dielectric function $[\epsilon(\vec{q}, \omega)]^{-1}$ via the fluctuation-dissipation theorem. The equations are solved self-consistently to determine $S(\vec{q})$ as originally suggested by Singwi *et al.*³⁻⁵

In Sec. II a brief discussion of the frequency moments of the spectral function of the density-response function is presented. The expression for the third frequency moment is then used to determine the form of the local-field correction.

In Sec. III we discuss the compressibility ratio and the coefficient of the leading term in the plasmon-dispersion relation, which are related to the long-wavelength limit of the local-field correction. Explicit results in the Hartree-Fock (HF) approximation are also presented. We obtain exactly the same value for the coefficient of the leading term in the plasmon-dispersion relation in the HF approximation in our theory as obtained by Nozières and Pines⁶ and Kanazawa *et al.*⁷ by an entirely dif-

ferent method.

In Sec. IV the results, based on a self-consistent calculation of the static structure factor, are given for the static-pair-correlation function, compressibility ratio, plasmon dispersion, and correlation energy of an electron liquid in the metallic density range.

Concluding remarks are presented in Sec. V.

II. THEORY

A. Generalities

The system of degenerate electrons immersed in a uniform neutralizing background of positive charge is described by the Hamiltonian

$$H = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_{\vec{k}}' \phi(\vec{k}) \{ \rho_{\vec{k}} \rho_{-\vec{k}}^\dagger - N \}, \quad (1)$$

where the first term is the kinetic energy of the electrons, the second term represents the Coulomb repulsion between them, and N is the number of electrons. The prime on the summation sign in the second term in Eq. (1) indicates that the $\vec{k}=0$ term should be omitted from the sum. The Fourier transform of the Coulomb potential is given by $\phi(\vec{k}) = 4\pi e^2/k^2$, and the density-fluctuation operator is defined as

$$\rho_{\vec{k}} = \sum_i e^{-i\vec{k} \cdot \vec{r}_i} . \quad (2)$$

The linear response of the system to a space- and time-dependent external probe which couples to the density fluctuation in the system is described through the density-response function. The density-response function is defined as the average of the retarded commutator^{8,9}

$$\chi(\vec{q}, t) = -i\theta(t) \langle [\rho_{\vec{q}}(t), \rho_{\vec{q}}^\dagger(0)] \rangle , \quad (3)$$

where $\theta(t)$ is the unit step function and the angular brackets denote the equilibrium ensemble average

appropriate to the system Hamiltonian (1). $\rho_{\vec{q}}(t)$ is the operator in the Heisenberg representation. In the theory of electron liquid it has been found most useful to introduce a wave-vector- and frequency-dependent dielectric function $\epsilon(\vec{q}, \omega)$ which is related to the Fourier transform $\chi(\vec{q}, \omega)$ of the density-response function $\chi(\vec{q}, t)$ by the relation

$$1/\epsilon(\vec{q}, \omega) - 1 = \phi(\vec{q})\chi(\vec{q}, \omega). \quad (4)$$

The dielectric function $\epsilon(\vec{q}, \omega)$ is a central quantity in the theory of metals. Many properties of metals can be discussed in terms of the dielectric function. Since these are already discussed in detail in the papers of Singwi *et al.*,³⁻⁵ we shall not repeat them here.

To discuss the moment relations it is very convenient to introduce the function $\chi_2(\vec{q}, t)$ defined as^{8,9}

$$\chi_2(\vec{q}, t) = -\frac{1}{2} \langle [\rho_{\vec{q}}(t), \rho_{\vec{q}}^\dagger(0)] \rangle; \quad (5)$$

its Fourier transform is given as

$$\chi_2(\vec{q}, t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega t} \chi''(\vec{q}, \omega), \quad (6)$$

where $\chi''(\vec{q}, \omega)$ is the imaginary part of $\chi(\vec{q}, \omega)$. Since $\chi(\vec{q}, t)$ in Eq. (3) is a retarded response function, $\chi(\vec{q}, \omega)$ is analytic in the upper half of the complex ω plane and $\chi''(\vec{q}, \omega)$ is an odd function of ω . Further, it follows that $\chi''(\vec{q}, \omega)$ is the spectral function of $\chi(\vec{q}, \omega)$, i. e.,

$$\chi(\vec{q}, \omega) = \int_{-\infty}^{+\infty} \frac{d\omega'}{\pi} \frac{\chi''(\vec{q}, \omega')}{\omega' - \omega - i\eta}, \quad (7)$$

where $\eta = 0^+$. The large- ω expansion of $\chi(\vec{q}, \omega)$ is obtained from Eq. (7) as

$$\chi(\vec{q}, \omega) = -\frac{\langle \omega^1 \rangle}{\omega^2} - \frac{\langle \omega^3 \rangle}{\omega^4} - O\left(\frac{1}{\omega^6}\right). \quad (8)$$

The coefficients in the asymptotic expansion of $\chi(\vec{q}, \omega)$ are the odd frequency moments of the spectral function $\chi''(\vec{q}, \omega)$; we define them as

$$\langle \omega^{2l-1} \rangle = \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \omega^{2l-1} \chi''(\vec{q}, \omega). \quad (9)$$

It is now easy to calculate the low-order moments or sum rules for the spectral function $\chi''(\vec{q}, \omega)$.

These may be obtained by differentiating Eq. (5) with respect to t and then putting $t=0$. Using Eqs. (5), (6), and (9), we obtain

$$\langle \omega^1 \rangle = \langle [[\rho_{\vec{q}}, H], \rho_{\vec{q}}^\dagger] \rangle = nq^2/m, \quad (10)$$

where m is the mass and n is the mean density of electrons. Equation (10) is the well-known f -sum rule. The third frequency moment of $\chi''(\vec{q}, \omega)$ is given as

$$\langle \omega^3 \rangle = \langle [[[[\rho_{\vec{q}}, H], H], H], \rho_{\vec{q}}^\dagger] \rangle$$

$$= -\langle [[[\rho_{\vec{q}}, H], H], [\rho_{\vec{q}}^\dagger, H]] \rangle. \quad (11)$$

It is straightforward to evaluate these commutators using the Hamiltonian (1). It may be mentioned here that in evaluating them one uses only the commutation relations of the position and momentum operators. The results are therefore independent of the statistics. The third moment is given for the electron liquid in the form

$$\langle \omega^3 \rangle = \frac{nq^2}{m} \left(\omega_q^2 + \frac{2q^2}{m} \langle T_{KE} \rangle + \frac{nq^2}{m} \phi(\vec{q}) \right) + \frac{1}{m} \sum_{\vec{k} \neq \vec{q}} (\vec{k} \cdot \hat{q})^2 \phi(\vec{k}) \{S(\vec{q} - \vec{k}) - S(\vec{k})\}, \quad (12)$$

where $S(\vec{k})$ is the usual static structure factor, $\omega_q = \hbar q^2/2m$, and \hat{q} denotes the unit vector. It may be noted that $\langle T_{KE} \rangle$ is the exact kinetic energy per electron. The result for the third moment was first derived by Puff.² We have also derived the expression for the fifth moment; it is very much complicated and shall be given elsewhere.¹⁰ For the sake of completeness we quote the fluctuation-dissipation theorem which relates the Fourier transform of the space- and time-dependent correlation function $S(\vec{q}, \omega)$ to $\chi''(\vec{q}, \omega)$. It is given as¹

$$S(\vec{q}, \omega) = -(\hbar/\pi n) (1 - e^{-\beta\hbar\omega})^{-1} \chi''(\vec{q}, \omega). \quad (13)$$

From Eq. (13) the so-called zeroth-moment sum rule can be written in terms of the dielectric function as

$$S(\vec{q}) = -\frac{\hbar q^2}{4\pi^2 n e^2} \int_{-\infty}^{+\infty} d\omega (1 - e^{-\beta\hbar\omega})_x^{-1} \times \text{Im} \left(\frac{1}{\epsilon(\vec{q}, \omega)} \right). \quad (14)$$

At temperature $T=0$, $(1 - e^{-\beta\hbar\omega})^{-1}$ is simply equal to unity.

B. Model for $\chi(\vec{q}, \omega)$

In the generalized random-phase approximation (GRPA) or effective-mean-field approximation, the expression for the density-response function is taken as¹

$$\chi(\vec{q}, \omega) = \frac{\chi_0(\vec{q}, \omega)}{1 - \psi(\vec{q})\chi_0(\vec{q}, \omega)}, \quad (15)$$

where $\psi(\vec{q})$ is the effective mean field and $\chi_0(\vec{q}, \omega)$ is the response of a noninteracting electron gas given by

$$\chi_0(\vec{q}, \omega) = \frac{1}{\hbar} \sum_{\vec{k}} \frac{n_{\vec{k}} - n_{\vec{k} + \vec{q}}}{\omega + \omega_{\vec{k}} - \omega_{\vec{k} + \vec{q}} + i\eta}, \quad (16)$$

where $n_{\vec{k}}$ are the usual fermion occupation numbers.

To examine the moments of the spectral function of the density-response function, one looks into the asymptotic large- ω expansion of $\chi(\vec{q}, \omega)$ from Eq.

(15). It can be written as

$$\chi(\vec{q}, \omega) = -\frac{nq^2}{m\omega^2} - \frac{nq^2}{m} \left(\omega_a^2 + \frac{2q^2}{m} \langle T_{KE} \rangle_f + \frac{nq^2}{m} \psi(\vec{q}) \right) \frac{1}{\omega^4} - O\left(\frac{1}{\omega^6}\right). \quad (17)$$

In obtaining Eq. (17) we have used the asymptotic expansion of $\chi_0(\vec{q}, \omega)$. Here $\langle T_{KE} \rangle_f$ is the kinetic energy per particle of a noninteracting electron gas. Using Eqs. (10) and (12) it can be easily seen from Eqs. (8) and (17) that first moment or the f -sum rule is automatically satisfied. Since it is connected to particle-number conservation, it is satisfied by any model which gives free particle behavior in the high-frequency limit. The third moment relation will be satisfied if

$$\chi(\vec{q}) = \phi(\vec{q}) [1 - G(\vec{q})], \quad (18)$$

where

$$G(\vec{q}) = -\frac{1}{4\pi n e^2} \sum_{\vec{k}} \{ [\hat{q} \cdot (\vec{k} + \vec{q})]^2 \phi(\vec{k} + \vec{q}) - (\hat{q} \cdot \vec{k})^2 \phi(\vec{k}) \} [S(\vec{k}) - 1]. \quad (19)$$

In obtaining the local-field correction $G(\vec{q})$ given in Eq. (19) we have ignored the difference between the exact kinetic energy and the kinetic energy of a noninteracting electron gas (i. e., correlation kinetic energy). The $G(\vec{q})$ in Eq. (19) can be written in a form suitable for numerical computation as

$$G(\vec{q}) = -\frac{1}{4\pi^2 n} \int_0^\infty dk k^2 [S(k) - 1] \times \left(\frac{5}{6} - \frac{k^2}{2q^2} + \frac{(k^2 - q^2)^2}{4kq^3} \ln \left| \frac{k+q}{k-q} \right| \right). \quad (20)$$

The function $G(\vec{q})$ is a functional of the static structure factor and will be determined using the fluctuation-dissipation theorem, as was first suggested by Singwi *et al.*³ Our expression for the dielectric function can be written in the usual form:

$$\epsilon(\vec{q}, \omega) = 1 + \frac{Q_0(\vec{q}, \omega)}{1 - G(\vec{q})Q_0(\vec{q}, \omega)}, \quad (21)$$

where

$$Q_0(\vec{q}, \omega) = -\phi(\vec{q})\chi_0(\vec{q}, \omega)$$

is the Lindhard function. Since the various properties and sum rules for the dielectric function have been discussed in detail by Vashishta and Singwi⁵ (see Sec. V, Ref. 5), we shall not repeat them here. The dielectric function given by Eq. (21) together with Eq. (20) for $G(\vec{q})$ satisfies all the necessary conditions. Equations (14) (at $T=0^\circ\text{K}$), (20), and (21) constitute the basic equations of this paper.

III. LONG-WAVELENGTH PROPERTIES AND HARTREE-FOCK LIMIT

A. Compressibility Ratio

The dielectric function (21) in the limit $\vec{q} \rightarrow 0$ and $\omega = 0$ has the form

$$\lim_{\vec{q} \rightarrow 0} \epsilon(\vec{q}, 0) = 1 + \frac{(q_{TF}/q)^2}{1 - \gamma(q_{TF}/q_F)^2}, \quad (22)$$

where q_{TF} and q_F are the Thomas-Fermi and Fermi wave vectors, respectively. From the compressibility sum rule one obtains

$$K_f/K = 1 - \gamma(q_{TF}/q_F)^2 = 1 - (4\lambda r_s/\pi)\gamma, \quad (23)$$

where K_f is the compressibility of the noninteracting electron gas and $\lambda = (4/9\pi)^{1/3}$. γ in (23) is related to the long-wavelength limit of $G(\vec{q})$ by

$$\lim_{\vec{q} \rightarrow 0} G(\vec{q}) \rightarrow \gamma(q/q_F)^2, \quad (24)$$

where

$$\gamma = \frac{2}{5}\bar{\gamma} \quad (25)$$

and

$$\bar{\gamma} = -(2q_F)^{-1} \int_0^\infty dk [S(k) - 1]. \quad (26)$$

B. Plasmon Dispersion

The dielectric function in the limit $\vec{q} = 0$ and finite ω has the form

$$\lim_{\vec{q} \rightarrow 0} \epsilon(\vec{q}, \omega) = 1 - \frac{\omega_p^2}{\omega^2} \left[1 + \frac{9}{5} \left(\frac{q}{q_{TF}} \right)^2 - \gamma \left(\frac{q}{q_F} \right)^2 \dots \right], \quad (27)$$

where ω_p is the plasma frequency. The plasmon dispersion in the long-wavelength limit is then

$$\omega_p(q) = \omega_p + \alpha \hbar q^2/m + \dots, \quad (28)$$

where

$$\frac{\alpha}{\alpha_{RPA}} = 1 - \frac{5}{9} \frac{4\lambda r_s}{\pi} \gamma \quad (29)$$

and

$$\alpha_{RPA} = 3\hbar q_F^2/10m\omega_p.$$

C. Hartree-Fock Limit

In Eq. (25) if the Hartree-Fock value of the structure factor $S(k)$ is used, we obtain from Eq. (26) and (25) $\bar{\gamma}_{HF} = \frac{3}{8}$ and $\gamma_{HF} = \frac{3}{20}$. It may be noticed that in the theory of Singwi *et al.*³ one also obtains $\bar{\gamma}_{HF} = \frac{3}{8}$. However, in their theory $\gamma = \bar{\gamma}$, whereas in our theory $\gamma = \frac{2}{5}\bar{\gamma}$. It is interesting to note that the value of α/α_{RPA} with our $\gamma_{HF} = \frac{3}{20}$ is the same as obtained by Nozières and Pines⁶ and Kanazawa *et al.*⁷ by entirely different methods. The compressibility ratio derived by differentiating the ground-state energy in the HF approximation corresponds to $\gamma = \frac{1}{4}$.¹¹

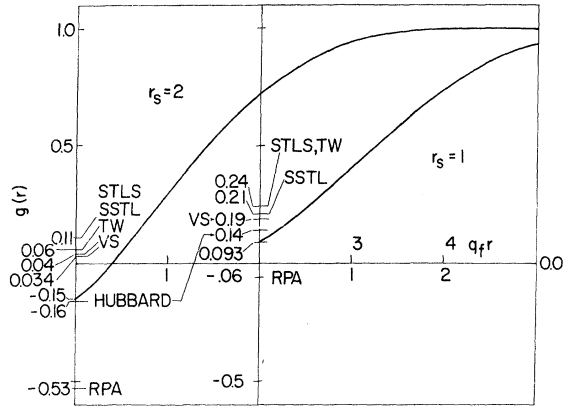


FIG. 1. Pair-correlation function $g(r)$ vs $q_f r$ for $r_s = 1$ and 2. Values of $g(0)$ in various theories are also marked.

Toigo and Woodruff¹² obtain the value of $\gamma = \frac{1}{4}$ from the long-wavelength limit of $G(\vec{q})$ in their theory. In a recent paper Vashishta and Singwi⁵ also get the value of $\gamma = \frac{1}{4}$ in the Hartree-Fock approximation. However, their self-consistent theory satisfies the compressibility sum rule *almost* exactly. In our case also $S(\vec{q})$ is determined self-consistently. Results of such calculations are described in the next section.

IV. CALCULATIONS AND RESULTS

Equations (14), (20), and (21) constitute the basic equations in our theory. The equations were solved on a digital computer. The procedure is similar to the one described by Singwi *et al.*³ About ten iterations were needed to obtain convergence in $G(\vec{q})$ to better than 0.1% accuracy. This implies a

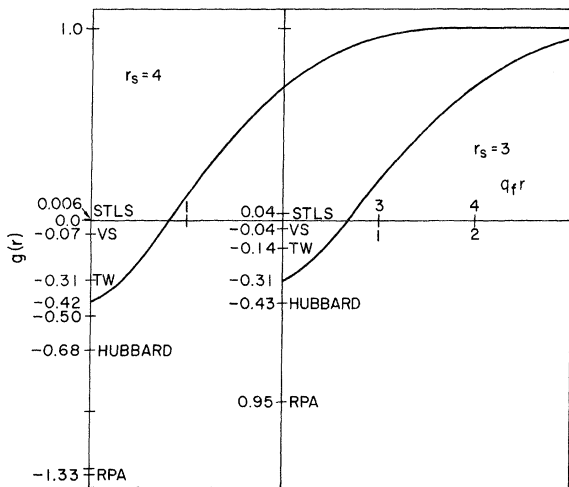


FIG. 2. Pair-correlation function $g(r)$ vs $q_f r$ for $r_s = 3$ and 4. Values of $g(0)$ in various theories are also marked.

TABLE I. Values of $\bar{\gamma}$.

| r_s | 1 | 2 | 3 | 4 | 5 | 6 |
|----------------|---------|---------|---------|---------|---------|---------|
| $\bar{\gamma}$ | 0.46920 | 0.51292 | 0.54302 | 0.56589 | 0.58417 | 0.59930 |

much higher accuracy in $S(\vec{q})$ used in the calculation of the properties described below.

A. Pair-Correlation Function

The pair-correlation function is given by

$$g(r) = 1 + \frac{3}{2r} \int_0^\infty q \sin(qr) [S(q) - 1] dq, \quad (30)$$

where q is in the units of the Fermi wave vector q_F and r is in units of q_F^{-1} . It is interesting to relate the $q \rightarrow \infty$ limit of the local field $G(\vec{q})$, which is a functional of $S(\vec{q})$, to the $\vec{r} \rightarrow 0$ limit of the pair-correlation function $g(\vec{r})$. In our theory the relation is

$$\lim_{\vec{q} \rightarrow \infty} G(\vec{q}) = \frac{2}{3} [1 - g(0)]. \quad (31)$$

This is different from similar relations found in the theory of Singwi *et al.*,^{3,4} e.g.,

$$G(\infty) = [1 - g(0)]. \quad (32)$$

In the theory of Vashishta and Singwi⁵ the corresponding relation reads

$$G(\infty) = \left(1 - \frac{2}{9} r_s \frac{d}{dr_s}\right) [1 - g(0)]. \quad (33)$$

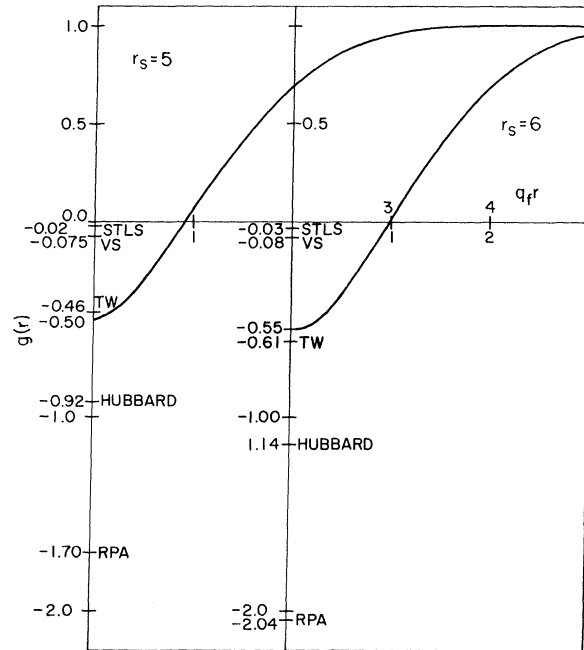


FIG. 3. Pair-correlation function $g(r)$ vs $q_f r$ for $r_s = 5$ and 6. Values of $g(0)$ in various theories are also marked.

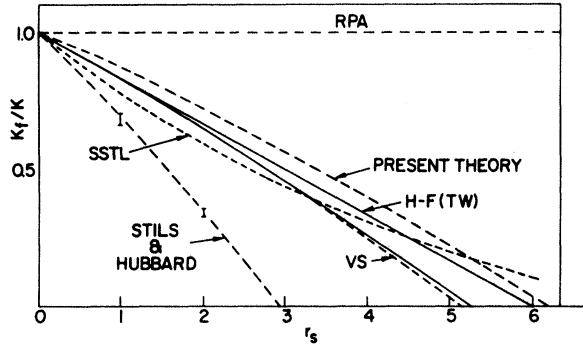


FIG. 4. Ratio between the free-electron compressibility and the compressibility of the electron liquid vs r_s . The unlabeled continuous wave is obtained by differentiation of the ground-state energy. The broken curve (labeled present theory) is obtained from Eq. (23). The continuous curve [labeled H-F (TW)] is obtained from differentiating the ground-state energy in the H-F approximation. The same curve is obtained in the theory of (Ref. 12) from the $\vec{q} \rightarrow 0$, $\omega = 0$ limit of $\epsilon(\vec{q}, \omega)$.

The values of $g(r)$ calculated from Eq. (30) by using the self-consistent values of $S(q)$ are shown in Figs. 1–3 for $r_s = 1$ to 6. Our values of $g(r)$ at small interparticle separation are negative for $r_s \geq 2$. Clearly for large r_s values (see Figs. 2 and 3) our $g(r)$ is poorer compared to the $g(r)$ in the theory of Singwi *et al.*^{3,4} and Vashishta and Singwi.⁵ Our $g(r)$ for small values of r_s is slightly inferior to that of Toigo and Woodruff,¹² but for large values of r_s (see Fig. 3, $r_s = 6$) our $g(r)$ is slightly better than that of Toigo and Woodruff.

B. Compressibility Ratio and Plasmon Dispersion

The expression for K/K_f and $\alpha/\alpha_{\text{RPA}}$ in Eqs. (23) and (29) have been evaluated using the value of

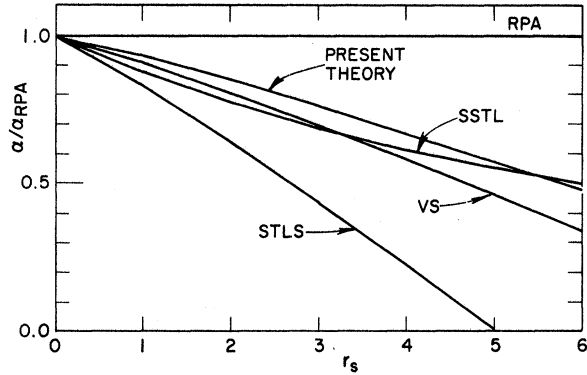


FIG. 5. Coefficient of the leading term in the plasmon-dispersion relation (in units of its RPA value) vs r_s . The curve labeled present theory is obtained from Eq. (29).

$\bar{\gamma}$ evaluated from Eq. (26) using the self-consistent values of $S(q)$. Table I gives the values of $\bar{\gamma}$ for $r_s = 1$ to 6. Figure 4 shows the plot of K_f/K versus r_s . The unmarked continuous curve is the compressibility ratio obtained by differentiating the ground-state energy. The broken curves stand for the $\vec{q} \rightarrow 0$, $\omega = 0$ limit of the dielectric function in various theories. The best compressibility sum rule is obtained in the theory of Vashishta and Singwi.⁵ Figure 5 shows $\alpha/\alpha_{\text{RPA}}$ as a function of r_s in various theories.

C. Correlation Energy

The correlation energy per particle can be written as³

$$\epsilon_{\text{corr}} = \frac{1}{r_s^2} \int_0^{r_s} \left[-\frac{4}{\pi} \left(\frac{9\pi}{4} \right)^{1/3} \bar{\gamma}(r_s') + 0.9163 \right] dr_s' \text{ Ry}, \quad (34)$$

TABLE II. Correlation energy (Ry/electron).

| r_s | 1 | 2 | 3 | 4 | 5 | 6 |
|---------------------------------|--------------------|--------------------|--------------------|--------------------|-------------------|--------------------|
| Present theory | -0.139 | -0.106 | -0.089 | -0.078 | -0.069 | -0.063 |
| Vashishta and Singwi | -0.130 | -0.098 | -0.081 | -0.070 | -0.062 | -0.056 |
| Singwi <i>et al.</i> (Ref. 4) | -0.125 | -0.097 | -0.080 | -0.070 | -0.063 | -0.057 |
| Singwi <i>et al.</i> (Ref. 3) | -0.124 | -0.092 | -0.075 | -0.064 | -0.056 | -0.050 |
| Hubbard | -0.131 | -0.102 | -0.086 | -0.076 | -0.069 | -0.064 |
| Nozières and Pines | -0.115 | -0.094 | -0.081 | -0.072 | -0.065 | -0.060 |
| RPA | -0.157 | -0.124 | -0.105 | -0.094 | -0.085 | -0.078 |
| Toigo and Woodruff ^a | -0.134 (-0.120) | -0.095 (-0.092) | -0.079 (-0.077) | -0.068 (-0.068) | 0.061 (-0.061) | -0.056 (-0.056) |

^aThe values in the parentheses in the last row are those calculated by us using the numerical values of $G(q)$ given by Toigo and Woodruff [Ref. 12 (1970)]. These values are different from those reported by these authors in Ref. 12 (1971).

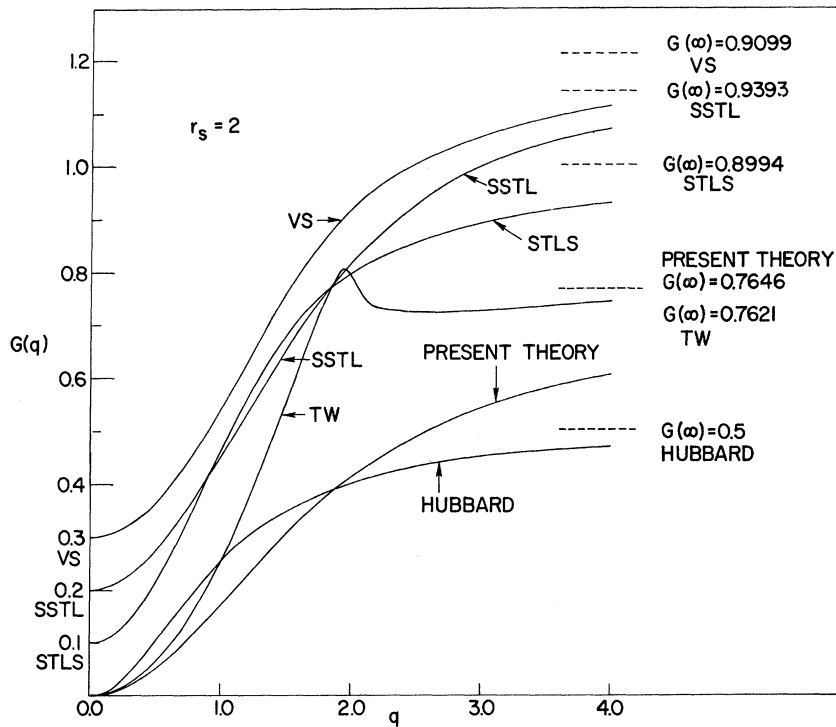


FIG. 6. Self-consistent value of the local field $G(q)$ vs q for $r_s=2$ in various theories. Here q is in units of q_f . The broken lines at the right-hand side of the figure represent the $q \rightarrow \infty$ limit of $G(q)$. Note the shift in the zero on the vertical axis by 0.1, 0.2, and 0.3 for STLS, SSTL, and VS, respectively.

where $\bar{\gamma}$ is defined in Eq. (26). It may be mentioned here that the Ferrell¹³ condition on the ground-state energy, which is equivalent to

$$\frac{d}{dr_s} \bar{\gamma}(r_s) \geq 0,$$

is satisfied by the values of $\bar{\gamma}$ in Table I. Values

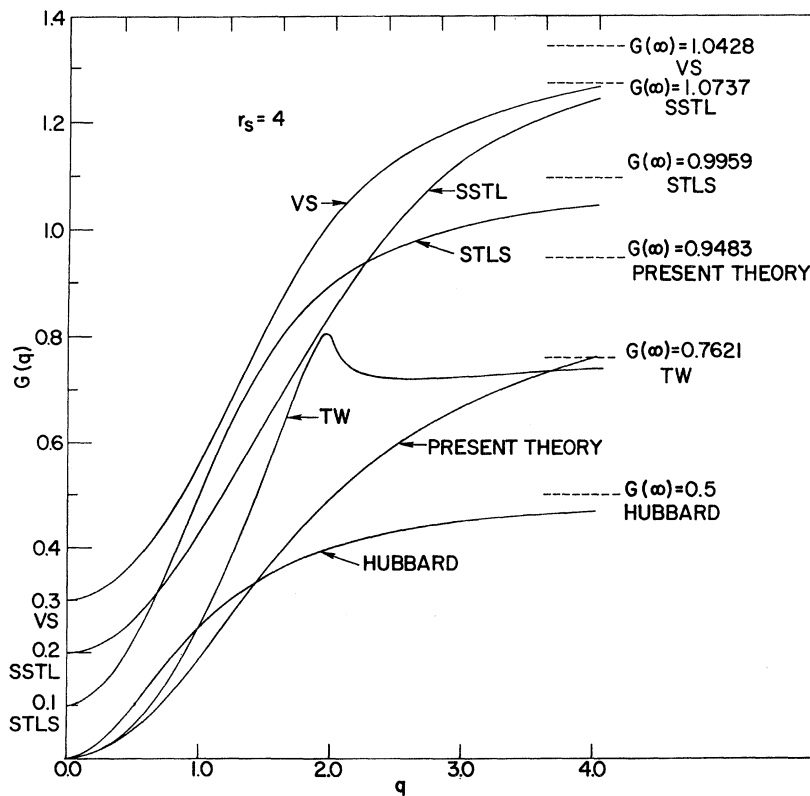


FIG. 7. Self-consistent value of the local field $G(q)$ vs q for $r_s=4$ in various theories. Here q is in units of q_f . The broken lines at the right-hand side of the figure represent the $q \rightarrow \infty$ limit of $G(q)$. Note the shift in the zero on the vertical axis by 0.1, 0.2, and 0.3 for STLS, SSTL, and VS, respectively.

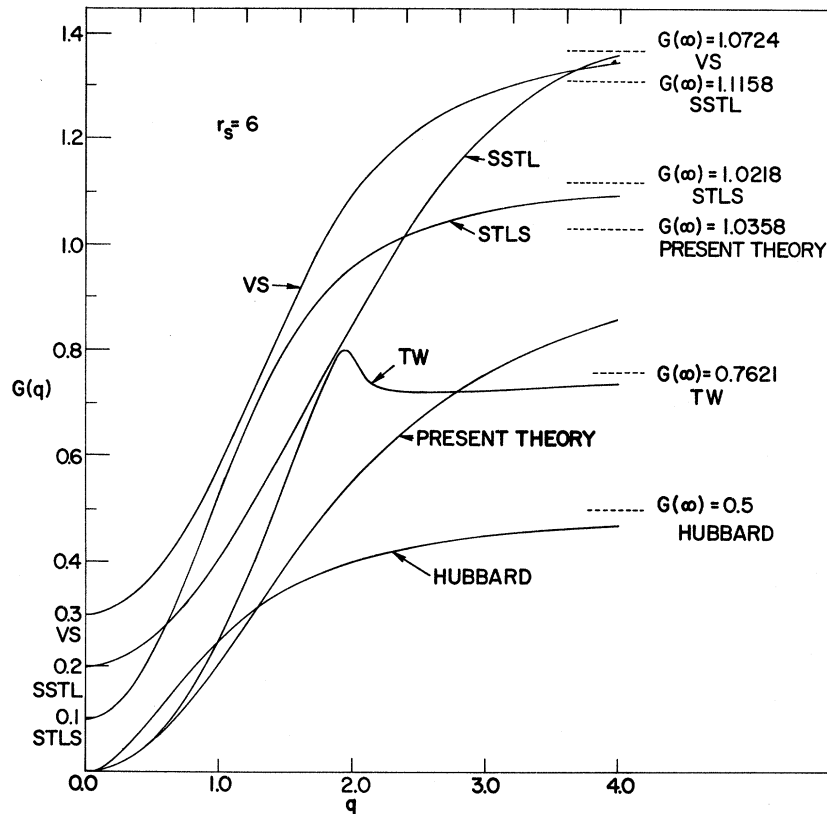


FIG. 8. Self-consistent value of the local field $G(q)$ vs q for $r_s=6$ in various theories. Here q is in units of q_F . The broken lines at the right-hand side of the figure represent the $q \rightarrow \infty$ limit of $G(q)$. Note the shift in the zero on the vertical axis by 0.1, 0.2, and 0.3 for STLS, SSTL, and VS, respectively.

of the correlation energy per particle are given in Table II together with the values in other theories.

D. Self-Consistent Local Field $G(\vec{q})$

For the sake of a comparison we have plotted $G(q)$ for different theories as a function of q for $r_s=2, 4, 6$ in Figs. 6, 7, and 8, respectively. Note that q is in units of the Fermi wave vector q_F . It might be mentioned here that $G(q)$ in the theories of Hubbard¹⁴ and Toigo and Woodruff¹² is independent of r_s . The $q \rightarrow \infty$ limits of $G(q)$ is marked by the broken lines at the right-hand side of the figures. Note the shift in the scale for $G(q)$ of Refs. 3, 4, and 5 marked as STLS, SSTL, and VS, respectively.

V. CONCLUDING REMARKS

The present theory has two encouraging features: (i) It satisfies the low-order frequency-moment relations, and (ii) in the HF case in the limit $\vec{q} \rightarrow \infty$, it yields $G_{\text{HF}}(\infty) = \frac{1}{3}$, a result which any exact theory in the HF limit should yield, as emphasized

by Geldart and Taylor.¹⁵ The discouraging aspect of the theory is that, in spite of the fact that our $G(\vec{q})$ is a function of $S(\vec{q})$ and the equation for $G(\vec{q})$ is solved self-consistently along with the fluctuation-dissipation theorem, it gives the values of the pair-correlation function, compressibility ratio, etc., which are nearly of the same quality as in the theory of Toigo and Woodruff.¹² The latter values are not so good when compared with the values obtained in the theories of Singwi *et al.*^{3,4} and Vashishta and Singwi.⁵ But by its very nature the theory should be better for high-frequency phenomenon ($\omega > \omega_p$).

ACKNOWLEDGMENTS

The authors are grateful to K. S. Singwi for suggesting the problem and continuous encouragement throughout the course of the work. One of the authors (P. Vashishta) acknowledges useful discussions with L. J. Sham, P. M. Marcus, and T. D. Schultz at IBM Thomas J. Watson Research Center.

*A preliminary report of this work has been presented in Nucl. Phys. Solid State (India) 13A, 81 (1970); Bull. Am. Phys. Soc. 17, 270 (1972).

[†]Work performed in part under the auspices of U. S. Atomic Energy Commission.

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VOLUME 7, NUMBER 8

15 APRIL 1973

Impurity Diamagnetism in Metals*

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(Received 31 October 1972)

The results of a broad experimental survey of impurity magnetism in liquid monovalent metal solvents is reported. As the impurity valence Z is increased, a giant impurity diamagnetism $\sim -150 \text{ cm}^3/\text{mole}$ emerges in alkali-metal solvents for $Z \sim 5$. The diamagnetism is explained by the concept of impurity ionicity developed in this paper, and the impurity structure is analyzed in detail using the present results and earlier spin-flip-scattering results of Slichter and his co-workers. There is quantitative agreement between the theory of fully ionic impurities and the experimental susceptibilities for higher-valence impurities. The broad scheme of impurity structure in monovalent metals is also clearly revealed. The susceptibility of Sn is studied as a function of host-electron density, and the transition from band to resonant $5p$ orbitals is identified. A solubility dip occurs, but the data are not precise enough to determine whether the transition has a one-electron or configurational character. It is further reported that the large diamagnetism of positive-valence solutes in Ag, previously studied by Henry and Rogers, disappears at the melting transition. No detailed analysis of this striking effect has been attempted, but the anomalous impurity diamagnetism in the solid is clearly associated with orbits involving the [111] necks on the Fermi surface.

I. INTRODUCTION

The nature of impurity states in metals has challenged experimental and theoretical investigations for fifty or more years. Much recent effort has been directed towards the study of transition-metal impurities, having unfilled d or f shells, in both "simple" metals and in more complex transition-metal host lattices. However, there remain major unresolved difficulties in our present understanding of valence impurities. These less complex solutes differ (in the atomic state) from host atoms only by the presence of extra neutralizing valence electrons. The difficulties relate to the emergence of bound impurity states, to the occurrence of ionicity among impurities in metals, and to certain striking phenomena connected with impurity diamagnetism and conduction-electron-spin resonance in metals. The central problem lies in the theoretical prediction and the experimental assignment of electronic structures to impurities in metals. In this paper we present the results of broad experimental studies, and their theoretical interpre-

tations. These yield a substantially more complete insight into the structure of valence impurities in simple metallic solvents. Preliminary accounts of several aspects of this work have been published elsewhere.¹

It has, of course, been understood since the pioneering work of Mott² that an impurity in solution must be neutralized by the electron gas, simply because metals conduct. The precise structure of the screening charge has, nevertheless, eluded description in most cases.³ From an experimental viewpoint there is the difficulty that the impurity structure must be defined throughout the range of host band energies and below, whereas most experiments are sensitive to a limited span of energies often near the Fermi energy E_F . There are also formidable theoretical difficulties. Foremost is the problem of self-consistency: The wave function of each electron in the system must be consistent with those of the remaining electrons, in the presence of the impurity perturbation. In the one-electron approximation, the wave functions fall into two categories. The first consists of localized or